[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE JOHNS HOPKINS UNIVERSITY]

# The Adsorption of Hydrogen on Tungsten[1]

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## Part I. Method and Experimental Results

The adsorption of hydrogen on various metals usually has been measured by determining the amount of hydrogen which disappears from the gas phase in presence of the adsorbent (volumetric method). Several authors, however, have used indirect methods by studying the changes which certain properties of the surfaces of metals (*e. g.*, the thermionic and photoelectric emission, the reflection of polarized light, the accommodation coefficients, the contact potentials, the electron diffraction patterns of the surface layers, etc.) undergo when they are covered with adsorbed gas. Most of these physical investigations led to the conclusion that hydrogen is very strongly adsorbed by the metals, forming already at low pressures (about $10^{-4}$ mm. of mercury at room temperature), a nearly complete surface film which contains one hydrogen atom per 1 or 2 atoms of the metal surface. This finding disagrees with direct adsorption measurements according to which the formation of a complete monolayer of the adsorbed gas requires much higher gas pressures.[2] J. K. Roberts who studied the adsorption of hydrogen on highly outgassed tungsten wires by an indirect method,[3] explains this discrepancy by assuming that, in the volumetric experiments, the metallic adsorbents were not sufficiently outgassed and still contained gaseous and other impurities which prevented the establishment of the actual adsorption equilibrium between the hydrogen and the metal.

An exact knowledge of the true adsorption equilibria is desirable not only for the theory of surface forces on metals, but also for a better understanding of the mechanism of many heterogeneous catalyses. The following study of the hydrogen adsorption on tungsten (powders) was carried out as a contribution to this main problem, particularly also with the aim of clearing up the discrepancy mentioned above. The volumetric method was used because it permits one to work with adsorbent surfaces of about $10^5$ sq. cm., allowing a much higher accuracy and the covering of a much wider range of pressures and temperatures than the physical methods mentioned above, in which, usually, specimens of only about 1 sq. cm. surface were employed. Prior to the adsorption runs, the surfaces of the tungsten powders were cleaned by an extensive, controlled outgassing procedure.

### Experimental Part

The main part of the measurements deals with the determination of the adsorption equilibria established on the tungsten powders, at various temperatures and hydrogen pressures. The measurements of adsorption and desorption rates are mentioned here only as far as it seems necessary in connection with the equilibrium measurements.

**The tungsten powders**[4] represented the metal in a state of fine dispersion and of high purity.[5] They differed in particle size, and, consequently, in their specific surfaces. Determinations of the specific surfaces of the powders were carried out by employing the experimental method (measurement of nitrogen-adsorption isotherms on the individual powders at low temperatures), and the evaluation method developed by P. H. Emmett, S. Brunauer and E. Teller.[6] Table I shows some of the surface values obtained in this way, together with the values calculated from the "average particle diameters," as determined by the manufacturer by means of a microscopic counting method. The surface values found by Emmett's method exceed, as is to be expected, the values calculated from the particle diameters, by a considerable factor.[7]

TABLE I

| | Surface values in sq. cm./g. | | |
|---|---|---|---|
| | of the original powder | | of the reduced and outgassed powder |
| Sample | calculated from particle sizes | measured by Emmett's method | measured by Emmett's method |
| 9799 | $0.47 \times 10^4$ | $2.79 \times 10^4$ | $2.08 \times 10^4$ |
| | | $2.85 \times 10^4$ | $2.05 \times 10^4$ |
| 9798 | $.32 \times 10^4$ | $1.01 \times 10^4$ | $0.72 \times 10^4$ |
| | | $1.01 \times 10^4$ | $.73 \times 10^4$ |
| 76–3 | $.27 \times 10^4$ | $0.58 \times 10^4$ | $.45 \times 10^4$ |

We see also from Table I the good reproducibility of the surface values obtained by measuring duplicate samples of the same powder-type, with Emmett's method. After the reduction and outgassing (described later), the surfaces have decreased, but to a well reproducible value.[8]

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[1] Original manuscript received April 27, 1942.

[2] See, *e. g.*, the survey in "Gases and Metals," by Colin J. Smithells, pp. 29–76 (John Wiley & Sons, Inc., New York, N. Y., 1937); and, for the particular case of hydrogen adsorption on tungsten, W. Frankenburger and A. Hodler, *Trans. Faraday Soc.*, **28**, 299 (1932).

[3] J. K. Roberts, *Proc. Roy. Soc.* (London), **A152**, 445, 447 (1935); **A161**, 141 (1937).

[4] The powders were supplied from the General Electric Co., Schenectady, N. Y., through the kindness of Dr. W. D. Coolidge, for which we want to express our sincere thanks. For general information on tungsten powders, compare C. J. Smithells, "Tungsten," D. Van Nostrand Co., New York, N. Y.

[5] According to information given by the manufacturer, the impurities consist approximately of 0.005% iron, 0.1% silica, 0.008% alkali.

[6] S. Brunauer and P. H. Emmett, THIS JOURNAL, **57**, 1754 (1935); P. H. Emmett and S. Brunauer, *ibid.*, **59**, 1553, 2682 (1937); S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938); P. H. Emmett and Thos. De Witt, *Ind. Eng. Chem.*, **13**, 28 (1941).

[7] Although the measurements of particle sizes are doubtless very useful for industrial purposes (distribution of particle sizes, relative surfaces), they cannot be used for calculating the *absolute* surface areas. Counting methods yield too low surface values because particles below a certain minimum size are not detected, because the "molecular roughness" of the surface is not accounted for, and because conglomerates of small particles might be registered as single larger particles.

[8] The values in Table I for reduced and outgassed powders have been obtained with different powder samples each of which was subjected to a separate reduction and outgassing.

The hydrogen for the reduction of the powders (pure "Electrolytic Hydrogen" of the Linde Co.) was purified by passing it through tubes filled with (1) shreds of pure copper (480°), (2) pellets of potassium hydroxide, (3) platinized asbestos (480°), and (4, 5) two freezing traps (−78° and −194°) both filled with copper pellets. For the adsorption measurements proper, it was subjected to a further purification by diffusion through a palladium tube at a temperature of about 380°. It was stored in a container of about 2000 cc. From time to time the latter was reëvacuated, flushed with hydrogen and refilled.

**Apparatus.**—From a known volume, filled with hydrogen at a certain temperature and pressure, the gas was expanded into the adsorption vessel (abbr. A.V.). The difference of the gas pressures established after the expansion into (a) the empty A.V., and (b) that obtained after the expansion into the A.V. containing the tungsten powder,[9] was the basis for calculating the amount of adsorbed gas. As the latter constitutes, particularly at higher pressures, and at higher temperatures, only a small fraction of the total amount of gas present, the calibrations had to be very accurate in order to lead to reliable, reproducible values. Generally, a satisfactory accuracy is reached in adsorption measurements, even for higher pressures, by making the volumes of the storage vessel, and especially the "dead space" of the adsorption vessel as small as possible. In the experiments described here, however, it was not possible to reduce the volumes under a certain size, because of the opposite demand of a thorough outgassing of the adsorbent. The latter requires the dimensions of the entire system not to be too small compared with the mean free path of gas molecules at very low pressures. Thus, the apparatus represented a compromise between two opposing requirements.

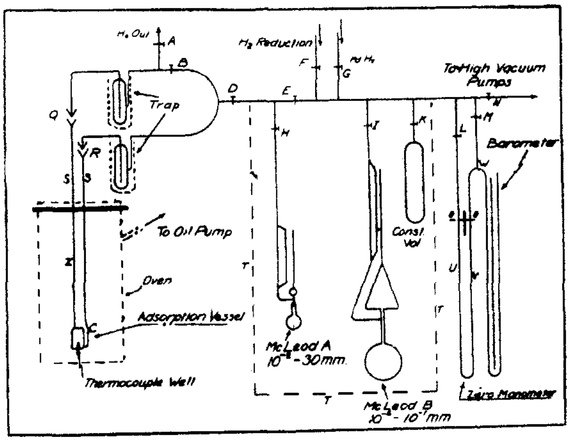

Fig. 1.—Scheme of adsorption apparatus.

Figure 1 shows the apparatus schematically. The adsorption vessel which contained the tungsten powder consisted of a cylindrical bulb (9 cc.) with an inlet tube C and an outlet tube Z. All tubes had an i. d. of 10 mm. or more except the lowest part (length 20 mm.) of C, which was constricted to 2 mm. i. d. (see Fig. 2). The adsorption vessel consisted of "Jena Supremax Glass" up to the points S-S where it was sealed to tubes of normal Pyrex glass, the latter being used for the rest of the apparatus. Through the two ground joints Q and R, the tubes led to the freezing traps. During the reduction of the powder, pure hydrogen entered through stopcock F, passed over E, D, R through the A.V., and left the system over Q and A. Stopcock B was closed during the reduction. The entire system was connected with the vacuum pumps (one Nelson Vacuum Oil Pump, two mercury diffusion pumps in series) and a large glass bottle as a "vacuum reservoir" over stopcock N.[9a] The "Constant Volume" served as a standard basis for the calibrations of the volumes of the Zero Manometer UV, McLeod gages A and B, and of the manifolds between the various stopcocks. During the adsorption runs, the McLeod gages served both as storage volumes for the palladium-purified hydrogen entering the system through O, and for measuring the pressure changes caused by the expansion of the hydrogen into A.V., through the stopcocks D and B. The McLeod gages were within the thermostat T. Figure 2 illustrates the construction of the adsorption vessel, A.V., and the heating system in detail. To avoid the collapse of the highly evacuated glass vessel A.V. at 750°, it was enclosed into a vacuum jacket VJ of stainless steel. The steel tube was closed at the bottom; at its upper end it had the horizontal disk D which could be flanged to another disk E, by means of the screws B and the rubber gasket RG. Disk E was fitted with a drum-shaped water cooler. The latter had, besides the water inlet and outlet, 3 vertical cylindrical holes into which the tubes Q and R, and the leads of the thermocouple Th (insulated by porcelain tubes) were sealed with Picein. The vacuum jacket VJ was heated by the surrounding oven (operated at 110 v., requiring about 4 amp. for 750°), and evacuated through the side-arm A, over a simple mercury manometer and a large glass bottle, by means of a separate Nelson Vacuum Oil Pump. The hot junction of the chromel–alumel thermocouple fitted into a vertical nose at the bottom of A.V.; the cold junction was kept in ice. The thermopotential was measured with a "Potentiometer Indicator" (Leeds and Northrup). The accuracy of the temperature measurements was checked from time to time by calibration of the thermocouple with baths of defined temperatures. The hot junction was covered with alundum cement to avoid its sticking to the hot glass walls. Preliminary measurements showed that the temperature gradient within the heated tungsten powder did not amount to more than about ±2.5° deviation from the average temperature.

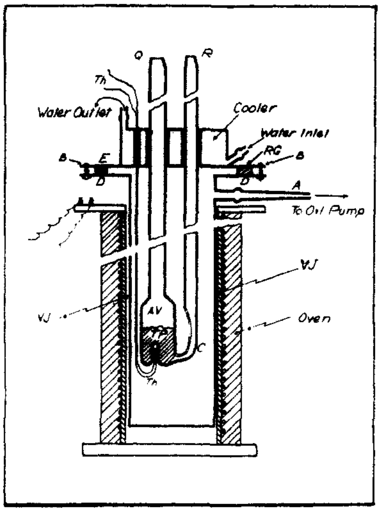

Fig. 2.—Adsorption vessel (A. V.).

**Calibrations.**—For measuring pressures between 10 and 750 mm., the U-tube UV, filled with mercury, was used as a zero manometer in connection with the barometer. The pressure in W was adjusted by admitting or withdrawing air until the mercury in U and V was at the same level. With the McLeod gage A (bulb volume about 3.5 cc., capillary diameter 2 mm.), pressures in the range of 5 ×

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[9] A correction has to be applied for the decrease of the free volume within the A.V., after its filling with tungsten powder. The volume of the powder was calculated from its weight and its density. The densities of the powders were determined by calibrations with helium, varying from 18.0 to 18.5, for the various powders.

[9a] There is another direct connection between the pumps and the part of the apparatus containing the A.V. This connection has been omitted in Fig. 1, in order to illustrate the principle of the set-up in its simplest form.

$10^{-2}$ to about 30 mm. were measured, and with the McLeod gage B (bulb vol. about 200 cc., capillary diameter about 1 mm.), pressures in the range of $5 \times 10^{-6}$ to about $2 \times 10^{-1}$ mm. Uniformity of the capillary diameters (±0.01 mm.) was checked by the method of the "travelling mercury drop," and by proving that successive expansions of hydrogen from each McLeod gage into the same evacuated volume resulted, over the entire lengths of the capillaries, in changes of the readings by the same ratio. The characteristic constant $\delta$ of each McLeod was determined by measuring with mercury (1) the volume of 1 mm. length of its capillary, and (2) the total volume of bulb + capillary, $\delta$ being equal to the ratio (1)/(2). The $\delta$-values were checked furthermore as follows: the same pressure was established in the zero manometer and in the McLeod A, within the range of their mutual overlapping (5 to 30 mm.). For several pressures in this region, the readings of McLeod A, evaluated with $\delta$, had to be identical with those of the Zero Manometer. The same procedure was applied to McLeod A and McLeod B, within the range of their overlapping ($5 \times 10^{-2}$ to $2 \times 10^{-1}$ mm.). The pressures measured with McLeod B were calculated by means of the usual formula $p = s^2\delta$ ($p$ = pressure in mm. Hg, $s$ = free length of capillary in reading position). For the larger pressures measured with McLeod A, the corrected formula: $p = s^2\delta/(1 - \epsilon s\delta)$ was used. $\epsilon$ is an individual constant depending only on the dimensions of the outer parts of the McLeod gage. Tables of $p$ as a function of $s$ were used for quick evaluations of the pressures measured with both McLeods.

As a basis for the calibration of the various volumes, the "Constant Volume" (see Fig. 1) was carefully calibrated with mercury. By expanding hydrogen from this vessel into the other parts of the apparatus, the "expansion coefficients" were determined. The expansions were repeatedly carried out at pressures ranging from $1 \times 10^{-3}$ mm. to about 750 mm.; and checks were added by other expansions (from one of the partial volumes into another, back into the "Constant Vol.," etc.). A similar procedure was adopted in determining expansion coefficients from McLeod A and McLeod B into the adsorption vessel, at all the temperatures (−194 to +750°) of this vessel employed in the adsorption runs. Throughout these calibrations, the cooling of the freezing traps with solid carbon dioxide,[9b] the heating of A.V. with the vacuum oven, and its immersion into low temperature baths to a fixed depth, were done in exactly the same way as in the adsorption measurements proper. For each temperature of A.V., the expansion coefficients were measured in the pressure range of $10^{-5}$ to 750 mm. (about 20 values per single temperature) because, at a given temperature, the expansion coefficient is not necessarily constant throughout the entire pressure range, on account of a possible "Knudsen effect."[10] The coefficients, however, proved to be constant for all the pressures at temperatures between −78 and 600°, indicating that the dimensions of the apparatus were large enough to prevent the appearance of a considerable Knudsen effect. Only with the A.V. at −194° did the expansion coefficient decrease, at pressures below $5 \times 10^{-2}$ mm., and reach a value, at $10^{-5}$ mm., which was smaller by 12% than the "high pressure value." For this pressure range, the expansion coefficient was tabled as a function of the gas pressure, and taken from the table for the evaluation of the hydrogen adsorption at −194°. Additional determinations of expansion coefficients were carried out by making successive inlets into A.V., first at low pressures, from McLeod B, and then, for increasingly higher pressures, from McLeod A, under retaining the gas of every last inlet within A.V. This method of "accumulated inlets" was used in the adsorption runs proper. In employing this method, the amount of gas left in A.V., from every previous inlet, has to be taken into account for the calculations. Although this method involves a transition from McLeod B to McLeod A, the values derived with it were in satisfactory agreement with those obtained from the single expansions. This proves that the volumes of the McLeods and of A.V. had been determined correctly, and that the transition from the pressures measured with McLeod B to those measured with McLeod A showed no discontinuity. The calibration of the apparatus, including all manometers, volumes and expansion coefficients required four to six weeks; it had to be repeated whenever changes in the apparatus proved to be necessary.

In spite of the care devoted to the calibrations, a slight possibility of errors remained. Errors in the calibration would result in a systematical falsification of all adsorption measurements made in the respective apparatus. To check this, a second apparatus was built along the same general principle as the first one, but with changed dimensions of the manometers, and changed volumes. The pumping system, ovens, etc., of the first and second apparatus were separate units. All calibrations of the second setup were made independently, starting with another barometer as the basis for calibrating the McLeods, and with another "Constant Volume" as the basis for calibrating the volumes and the expansion coefficients.

It might be mentioned here that adsorption measurements carried out on the same type of tungsten powder gave, in both set-ups, close agreement within the entire range of temperatures and pressures. This proves that the results were not falsified by a systematic error in the calibrations, and that the degassing of a given tungsten powder in different systems, if carried out in the same way, results in specimens of the same adsorbing properties.

**Preparation of the Tungsten Powders.**—The aim of the treatment of the tungsten-powders was to free, in a reproducible way, their surfaces from all adsorbed gases. Preliminary studies showed that the necessary purity of the metal surfaces could only be reached and maintained when the entire vacuum system was kept free from volatile impurities. The stopcocks were greased with "Apiezon N," which is recommended as having a negligible vapor pressure. The ground joints Q and R which had to be separated for emptying and refilling A.V., were tightened with "Ether Resin" which, if not overheated, evolves much less vapor than Picein and similar cements. In addition to this, it proved to be necessary to insert the freezing traps between A.V. and the stopcocks, and to keep these traps cooled with solid carbon dioxide throughout the experiments with a given tungsten sample. Various types of glasses were checked regarding their gas evolution at 750°, into a high vacuum, after a previous treatment with hydrogen at 750°. The smallest gas evolution was observed with "Jena Supremax Glass" which, evidently, does not dissolve any hydrogen at higher temperatures.[11] The adsorption vessel was thoroughly cleaned with aqua regia, cleaning solution and distilled water, whenever it had to be taken off for refilling. At the same opportunity, the freezing traps were torched out, with an air stream passing through. After cleaning, the A.V. was attached to the apparatus, thoroughly evacuated and baked out for several hours at 750°, then taken off, filled with a weighed amount of tungsten powder, and again joined to the apparatus. As it is likely that the particles of the tungsten powders have a layer of adsorbed oxygen, the powders were reduced with pure hydrogen at 750°, previous to the outgassing. This treatment, carried out with hydrogen of atmospheric pressure, flowing at a rate of 30 l./hr., was continued, without interruption, for a period of twenty-four to forty hours.[12] The outgassing

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(9b) Only for the measurements made with the tungsten powder cooled to −194° and −72° the freezing traps were kept in liquid nitrogen. The calibration for these temperatures were made, accordingly, with the traps immersed in liquid nitrogen.

(10) M. Knudsen, *Ann. Physik*, **28**, 75 (1909); **31**, 205, 633 (1910); **33**, 1435 (1910); **34**, 593 (1911); **35**, 389 (1911). In hot-cold tubes with diameters small compared with the mean free path, the pressures in the hot and cold part are: $p_h/p_c = \sqrt{T_h/T_c}$.

(11) Besides, this glass had the following advantages: it can be heated to 780°, for many hours, under a pressure difference of 1 atm., without any measurable deformation. It can be sealed to ordinary Pyrex glass Its disadvantage: it is inferior to Pyrex in resistance against sudden changes in temperature.

(12) In the course of the experiments, the reduction time of forty hours was cut down to twenty-four hours, after it was found that it did not change the adsorptive properties of the powders.

consisted in heating the powder in a high vacuum at 750°, under continuous pumping. This treatment took on the average about thirty-five to fifty hours, and was interrupted by 4 to 5 periods during which the powder, cooled to room temperature, stood overnight (for sixteen to eighteen hours) in the evacuated adsorption vessel. During the entire outgassing, including the overnight periods, the freezing traps were kept in solid carbon dioxide.[13] Two kinds of checks were employed to judge the progress of the outgassing and the final state of the powder. The "Closed Stopcock Values" (abbr. C. S. V.), *i. e.*, determinations of the amount of gas, evolved per minute from the powder at 750°, into a high vacuum, were determined by closing A.V. + McLeod B off from the mercury pumps, and registering every five minutes, over a period of fifteen minutes, the pressure being built up in McLeod B. With progressive outgassing, these C. S. V.'s decreased continuously. Whenever the powder was cooled down to room temperature for the "overnight period," the gas evolution became negligible: the pressure in A.V. decreased to a value $<5 \times 10^{-6}$ mm., and remained, even after sixteen hours of standing overnight, below $10^{-5}$ mm. After the overnight period, the second check was regularly carried out. The powder was gradually heated from room temperature to 750°. With the rising temperature, it evolved an increasing amount of gas which was collected and measured in the volume A.V. + McLeod B. The quantity of gas after the temperature had reached 750°, was appreciable, and was called the "Overnight Value" (abbr. O. V.). The latter is, even more than the C. S. V., significant for the state of the outgassing of the powder: it is the smaller the farther the outgassing has proceeded (compare Table II). After a treatment of about fifty hours at 750° in a high vacuum, further continuation of the outgassing, even for long periods, created no further decrease of the closed stopcock values and overnight values (C. S. V. = about $6 \times 10^{-11}$ mole/min., O. V. = about $2.5 \times 10^{-8}$ mole in eighteen hours). As the amounts of gas taken up by the tungsten samples during the adsorption runs lie within the range of $4 \times 10^{-7}$ to $4 \times 10^{-5}$ mole, the small residual gas evolution (C. S. V. at 750° = $6 \times 10^{-11}$ mole/min.) does not interfere with the adsorption measurements, particularly if we consider that most of the adsorption measurements are made at 600° and below, where the gas evolution is still smaller, by at least one order of magnitude, than at 750°. It is likely that the outgassing actually created bare surfaces of the powder particles, because: (1) the final values reached were close to the outgassing values of the empty adsorption vessel,[14] (2) continuation of the outgassing beyond the stage of steady C. S. V.'s and O. V.'s did not increase further the adsorptive capacities of the powders, and (3) the isotherms measured on different specimens of the same powder showed a good reproducibility. Taken alone, none of these three factors presents conclusive evidence for completeness of the outgassing. Combined, however, they make it very likely that the adsorption was measured on reasonably clean tungsten surfaces. We shall see that the values obtained in our measurements represent a further proof: they lie close to the values obtained, by other authors, with the methods of electron diffraction and measurements of adsorption heats, on metal surfaces which had been outgassed at temperatures around 2000°, in a high vacuum.

TABLE II

OUTGASSING SCHEDULE OF 11.8 g. OF TUNGSTEN POWDER 9798, AFTER A TWENTY-FOUR-HOURS REDUCTION WITH PURE HYDROGEN

| Total time of outgassing at 750° (in min.) | Gas evolution (in mole/min.) in high vacuum at 750° ("C. S. V.") | Length of overnight period (in min.), powder at room temp. in high vacuum | Gas collected from powder, after overnight period, if powder is heated up to 750° (in mole) ("O. V.") |
|---|---|---|---|
| 10 | $1.3 \times 10^{-7}$ | | |
| 100 | $4.2 \times 10^{-8}$ | | |
| | | 1080 | $4.8 \times 10^{-7}$ |
| 220 | $2.2 \times 10^{-9}$ | | |
| 340 | $1.5 \times 10^{-9}$ | | |
| 460 | $1.2 \times 10^{-9}$ | | |
| | | 1080 | $2.4 \times 10^{-7}$ |
| 620 | $7.6 \times 10^{-10}$ | | |
| 810 | $6.7 \times 10^{-10}$ | | |
| | | 1140 | $8.9 \times 10^{-8}$ |
| 1360 | $4.5 \times 10^{-10}$ | | |
| | | 2580 | $16.0 \times 10^{-8}$ |
| 1900 | $3.0 \times 10^{-10}$ | | |
| | | 1080 | $4.4 \times 10^{-8}$ |
| 2350 | $6.2 \times 10^{-11}$ | | |
| | | 1200 | $2.6 \times 10^{-8}$ |
| 2820 | $6.1 \times 10^{-11}$ | | |
| | | 1140 | $2.4 \times 10^{-8}$ |

The outgassing schedule of other powder samples (9798) is very similar, proving a good reproducibility of the process.

**The General Principle of the Adsorption Measurements.**—The method of "accumulated inlets" has already been mentioned. It is illustrated by the data of a single run, in Table III. The equilibria were determined, over the entire range of pressures ($10^{-5}$ to 30 mm.), for the various temperatures (−194 to 750°). Separate runs of accumulated inlets, each carried out at one single temperature, proved to be inadequate within the temperature range from −194 up to about 100°. When, at these lower temperatures, a new quantity of hydrogen was admitted into the adsorption vessel, the uptake of gas by the powder was only fast for an initial period,[15] followed by a slow decrease of pressure which continued for many (twelve to thirty) hours. A steady value is reached, at these low temperatures, only after a long waiting time. Besides the waste of time, this procedure is affected with the uncertainty as to whether the final values reached correspond to the true equilibria, or only to points at which the approach to the equilibrium has become extremely slow. Steady values were, however, obtained instantaneously when the tungsten powder was cooled down from higher to lower temperatures, in presence of the hydrogen. Hence, the following procedure was adopted: (1) inlet at 600°, measurement of adsorption, (2) cooling down step by step to 500, 400, ... to −194°, and measurement of adsorption at each temperature, (3) heating up to 600°, rechecking the adsorption values at the single temperatures, and repetition of this cycle after the next inlet, *i. e.*, at a higher pressure (comp. Table III). The equilibrium values obtained with increasing temperature checked regularly very well (within 0 to 5%) with those obtained while decreasing the temperature, even if the powder had been kept, in the meantime, for many hours at room temperature between the reversals of the temperature change. This proves that, with this method, the equilibria were established in a very short time, and that any additional gas evolution from the powder, the glass walls, etc., is too small to interfere with the adsorption measurements at the pressures and temperatures covered by our experiments. After a series of this type had given various points of the isotherms at different temperatures, the powder sample usually was outgassed again.[16] As soon as the final C. S. V. and O. V. outgassing values were reached again, new adsorption runs were carried out. In most of these repeated runs, very good agreement with the previous measurements was obtained. This indicates again that the state of outgassing can be reproduced, and, with it, the adsorptive properties of the tungsten powder. Similarly, a fresh sample of a given type of tungsten powder, after having

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(13) Only in the measurements with the adsorbent at −73 and at −194°, the traps were cooled with liquid nitrogen. Special calibrations were made for this range.

(14) This was checked by special runs with the empty adsorption vessel. The C. S. V.'s as well as the O. V.'s reached in these blank runs were only slightly lower than those obtained in presence of the tungsten powders, at the end of the outgassing process.

(15) The uptake in this initial period corresponds to about 75 to 95% of the amount taken up at the "true equilibrium."

(16) In some cases, also, a new reduction of the powder was carried out, followed by outgassing.

TABLE III

ADSORPTION RUN (NO. 27) WITH 12.52 g. OF TUNGSTEN POWDER 9798 (UNITS OF ADSORBED HYDROGEN EXPRESSED IN $10^{-6}$ MOLE (= $2.24 \times 10^{-2}$ cc. AT 0°, 760 mm.))

| No. of inlet | Temp. in °C. | Left in A. V. from previous admission: Adsorbed on powder | Left in A. V. from previous admission: In gas space | New portion expanded from storage in McLeod's into A.V. | Sum of the portions admitted to the powder in this and in the previous admissions | Amount of gas left in space of McLeod and of A.V., after adsorption of remainder on the tungsten-powder | Amount of adsorbed hydrogen: On total powder sample (in $10^{-6}$ mole) | Amount of adsorbed hydrogen: Per 1 g. of powder | Amount of adsorbed hydrogen: Per 1 sq. cm. of powder surface (in $10^{-12}$ mole) | Equilibrium pressures, in mm. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|  | 600 | .. | .... | 1.31 | 1.31 | 0.82 | 0.49 | 0.039 | 5.4 | $2.95 \times 10^{-2}$ |
| 1 | 500 | .. | .... |  |  | .28 | 1.03 | .082 | 11.3 | $1.00 \times 10^{-2}$ |
|  | 400 | .. | .... |  |  | .02 | 1.29 | .103 | 14.1 | $6.01 \times 10^{-4}$ |
| Stepwise increase of temperature to 600° yielded values which checked the adsorption values of inlet 1 |  |  |  |  |  |  |  |  |  |  |
|  | 600 | 0.49 | 0.20 | 5.27 | 5.96 | 4.99 | 0.97 | 0.077 | 10.5 | $1.80 \times 10^{-1}$ |
|  | 500 |  |  |  |  | 3.55 | 2.41 | .193 | 26.5 | $1.27 \times 10^{-1}$ |
| 2 | 400 |  |  |  |  | 1.67 | 4.29 | .343 | 47.1 | $5.98 \times 10^{-2}$ |
|  | 300 |  |  |  |  | 0.14 | 5.82 | .465 | 63.9 | $5.05 \times 10^{-3}$ |
|  | 200 |  |  |  |  | 0.001 | 5.96 | .477 | 65.5 | $2.11 \times 10^{-5}$ |
| Stepwise increase of temperature to 600° yielded values which checked the adsorption values of inlet 2 |  |  |  |  |  |  |  |  |  |  |
|  | 600 | 0.97 | 1.47 | 20.03 | 22.47 | 20.84 | 1.63 | 0.122 | 16.8 | $7.39 \times 10^{-1}$ |
|  | 500 |  |  |  |  | 18.54 | 3.94 | .314 | 43.1 | $6.61 \times 10^{-1}$ |
|  | 400 |  |  |  |  | 14.96 | 7.51 | .600 | 82.4 | $5.33 \times 10^{-1}$ |
| 3 | 300 |  |  |  |  | 11.39 | 11.08 | .885 | 121.6 | $4.04 \times 10^{-1}$ |
|  | 200 |  |  |  |  | 7.42 | 15.05 | 1.202 | 165.1 | $2.62 \times 10^{-1}$ |
|  | 100 |  |  |  |  | 2.64 | 19.83 | 1.585 | 217.7 | $9.25 \times 10^{-2}$ |
|  | 0 |  |  |  |  | 0.04 | 22.43 | 1.792 | 246.1 | $1.51 \times 10^{-3}$ |
|  | − 73 |  |  |  |  | 0.001 | 22.47 | 1.795 | 246.6 | $5 \times 10^{-6}$ |
| Stepwise increase of temperature to 600° yielded values which checked the adsorption values of inlet 3 |  |  |  |  |  |  |  |  |  |  |
| Inlets 4, 5, and 6 omitted, for the sake of brevity |  |  |  |  |  |  |  |  |  |  |
|  | 600 | 6.29 | 101.36 | 745.40 | 853.05 | 842.83 | 10.22 | 0.816 | 112.1 | 30.13 |
|  | 500 |  |  |  |  | 839.00 | 14.05 | 1.122 | 154.1 | 29.92 |
|  | 400 |  |  |  |  | 833.60 | 19.45 | 1.553 | 213.4 | 29.62 |
|  | 300 |  |  |  |  | 829.54 | 23.51 | 1.873 | 257.3 | 29.38 |
| 7 | 200 |  |  |  |  | 825.68 | 27.37 | 2.186 | 300.3 | 29.10 |
|  | 100 |  |  |  |  | 820.62 | 32.43 | 2.590 | 355.8 | 28.75 |
|  | 0 |  |  |  |  | 818.00 | 35.05 | 2.799 | 384.5 | 28.14 |
|  | − 73 |  |  |  |  | 815.90 | 37.15 | 2.967 | 408.6 | 27.50 |
|  | −194 |  |  |  |  | 809.20 | 43.85 | 3.502 | 481.1 | 24.14 |

been properly reduced and outgassed, gave adsorption values in good agreement with those obtained by repeated runs with another sample of the same type. This applies to measurements in both apparatus, although they were based on independent calibrations.

**The limits** of error in the adsorption experiments result from various sources such as from errors in the calibrations, in the reading of the McLeods, and of the temperatures and from changes of the powders such as sintering during the measurements, deviations in the state of outgassing, etc. In calculating the limits of error, it has to be considered that, in the method of accumulated inlets, errors in pressure readings are interconnected with each other, in the course of a single run, and that deviations of the powder temperature create very different errors in the calculation of the amounts of hydrogen adsorbed depending upon the range of pressure and temperature in which they occur. Generally, the errors are the larger, the smaller the ratio (adsorbed amount of gas)/(total amount of gas), *i. e.*, they increase with increasing temperature and pressure.[17] Table IV gives an approximate calculation of the limits of error, in the amounts adsorbed, for certain pressure and temperature ranges. The calculation is based on the average deviations of the amount of adsorbed gas from its "true" value caused by the combination of the single types of possible errors.[18]

## Experimental Results

Most of the adsorption runs were made with the tungsten powder 9798. The reproducibility of the isotherms was checked by (1) using the same powder specimen in repeated runs, (2) using various specimens of the same powder type in the same apparatus, and (3) using various specimens of the same powder type in the second apparatus.

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(17) There is also an increase in the region of low pressures due to the very pronounced change of the adsorbed amounts, in this range, at practically the same pressure, with even slight changes of the temperature.

(18) The latter were derived from experimental determinations of the different average errors, *e. g.*, on series of measuring the same pressure with the McLeod's, on comparative measurements of the surface values of different powders which had been used for adsorption runs, etc. In doubtful cases the upper limits of the deviations were used for evaluation of the limits of error in determining the adsorbed amounts of hydrogen.

TABLE IV

LIMITS OF ERROR IN THE ADSORPTION MEASUREMENTS

| Temp. (in °C.) | Pressure ranges(in log of mm). | Single average errors of adsorbed amounts (in %), caused by: | | | | Total average error, % | |
|---|---|---|---|---|---|---|---|
| | | Error in determin. pressure | Error in determin. temp. of powder | Error in calibrat. volumes | Change in powder | Calcd. from single errors | Obs. as av. dev. of exptl. points |
| | − 3 to −2 | 0.15 | 2 | 0.1 | 4 | ± 6.25 | ±4 |
| | − 2 to −1 | 0.10 | 1.5 | .1 | 4 | 5.7 | 3.5 |
| 600 | 0 to 0.7 | 3.5 | 1.0 | .2 | 4 | 8.7 | 5.5 |
| | 0.7 to 1.1 | 4.0 | 0.8 | .4 | 4 | 9.2 | 6.5 |
| | 1.3 to 1.5 | 5.0 | .6 | .7 | 4 | 10.3 | 7.0 |
| | − 5 to −4 | 0.6 | 1.0 | .1 | 4 | 5.7 | 2.5 |
| | − 4 to −2 | .5 | 0.7 | .1 | 4 | 5.3 | 2.0 |
| 300 | − 1 to 0 | .4 | 1.0 | .2 | 4 | 5.6 | 2.0 |
| | 0.7 to 1.2 | 1.7 | 0.6 | .4 | 4 | 6.7 | 2.8 |
| | 1.3 to 1.5 | 2.2 | .4 | .6 | 4 | 7.2 | 3.0 |
| | − 5 to −4 | 0.5 | .6 | .1 | 4 | 5.2 | 2.8 |
| | − 4 to −2 | .2 | .3 | .1 | 4 | 4.6 | 2.8 |
| 0 | − 1 to 0 | .4 | 1.4 | .2 | 4 | 6.0 | 3.3 |
| | 0.7 to 1.2 | 1.0 | 0.3 | .4 | 4 | 5.7 | 3.2 |
| | 1.3 to 1.5 | .3 | .2 | .5 | 4 | 5.0 | 3.2 |

As the measurements covered a pressure range of 6 orders of magnitude ($10^{-5}$ to 30 mm.) and temperatures between −194 and 750°, the usual way of plotting isotherms ($A$ = adsorbed amount *vs.* $p$ = pressure) can, necessarily, represent only a fraction of the experimental results (only 2 orders of magnitude). Figure 3 is such a plot of isotherms obtained with powder 9798 as adsorbent, within the range of about 0.1 to 30 mm

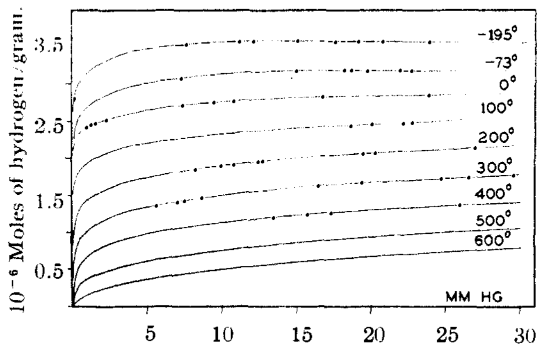

Fig. 3.—Adsorption isotherms for tungsten powder 9798.

The isotherms show a considerable increase of $A$ with decreasing temperatures and almost[19] parallel trends at the higher pressures. Figure 3 seems, furthermore, to indicate that at room temperature saturation of the adsorption is reached already at a pressure of about 5 to 10 mm. The true character of the isotherm is by far better revealed by another method of plotting the experimental points: The adsorption values measured within the total range of pressures and temperatures can be shown by a graph in which, instead of plotting $A$ against $p$, log $A$ is plotted against log $p$.[20] Figure 4 represents such a logarithmic plot of the hydrogen adsorption isotherms on powder 9798. For the sake of simplicity, Fig. 4 shows the experimental points of only two runs. Actually, about 30 runs were made with powder 9798 as adsorbent. The experimental points of all these runs are, with very few exceptions, scattered around the mean values with deviations not larger than those listed in the last column of Table IV.

The unexpected result of these adsorption measurements is that the isotherms, plotted in the logarithmic graph, are—over the entire range of temperatures and pressures studied with powder 9798—almost straight lines. Only a thorough examination of the experimental points by means of the method of the least squares shows that the logarithmic isotherms have a very slight tendency to become flatter, at higher coverings of the adsorbent. The corresponding changes of the isothermic slopes are small. Thus, the slopes $\alpha$ = log $p$/log $A$ of the 300, 400, 500 and 600 isotherms (powder 9798) change, respectively, from $\alpha$ = 5.42, 4.02, 2.98 and 2.24, for $A = 3 \times 10^{-8}$ mole $H_2$/g., to 5.80, 4.35, 3.08 and 2.38 for the about 30 times larger surface covering of $A = 100 \times 10^{-8}$ mole $H_2$/g. These changes of the slopes just exceed the limits of experimental errors, and are too small to show up on our logarithmic graph, as distinct deviations from the straightness of the isotherms. The lines drawn through the experimental points can be extrapolated as straight lines beyond the range of our measurements, to higher pressures and higher adsorbed amounts. They intersect each other in one common point which, for powder 9798, corresponds to log $A$ = 0.56, or $A = 360 \times 10^{-8}$ mole $H_2$/g. The conclusion that this amount of adsorbed gas $s$ is equivalent to the saturation value of the adsorption, is not justified, in view of the flattening of the isotherms. A theoretical discussion will be presented in the following paper in which the changes of the slopes are taken into account, and in which a more adequate extrapolation of the isotherms to higher surface coverings is carried out. This extrapolation leads to the "true saturation value," $S = 660 \times 10^{-8}$ mole $H_2$/g., for powder 9798.

Tungsten powder 9799, which served as adsorbent in a number of analogous adsorption runs, had the larger specific surface of 28, 100 sq. cm./g. before, and of 20, 700 sq. cm.$^2$/g. after the outgassing. The log $A$/log $p$ plot for this powder is very similar to the plot obtained for powder 9798: the slopes of the logarithmic isotherms as well as their flattening at higher surface coverings are, within the limits of experimental errors, the same for both powders. The point of common intersection, $s$, of the roughly extrapolated isotherms lies at $A = 1000 \times 10^{-8}$ mole $H_2$/g., and the calculated value for $S$, the "true" saturation value,

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(19) From this plot, it cannot be seen whether the isotherms are strictly parallel at higher pressures, or not. Figure 4, however, shows that they are actually slightly convergent, and that they would intersect at about 1500 mm. pressure.

(20) $A$ is measured in units of $1 \times 10^{-8}$ mole $H_2$/g., $p$ in mm.

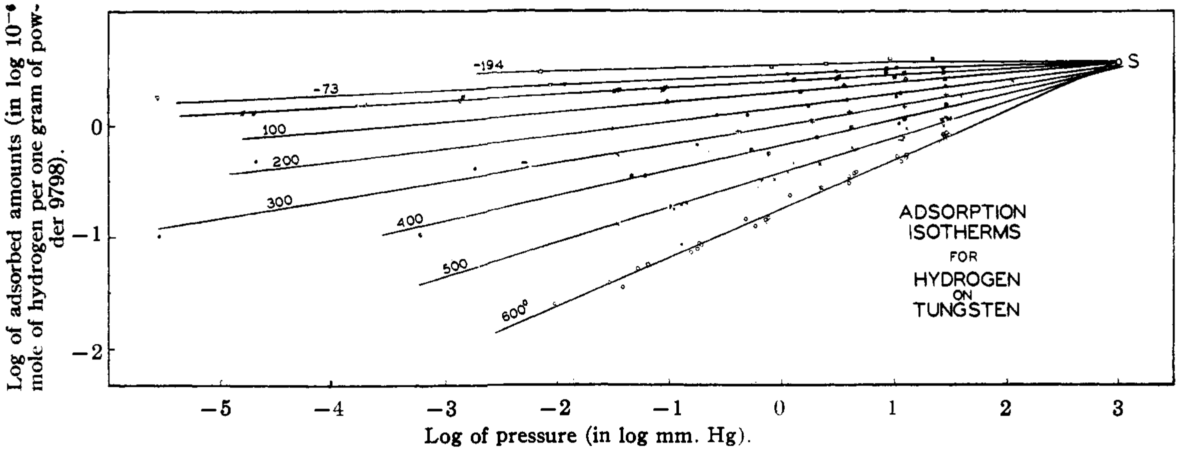

Fig. 4.—Logarithmic isotherms for tungsten powder 9798.

at 1820 × $10^{-8}$ mole $H_2$/g. These values exceed the corresponding values for powder 9798 by a factor of 2.76. The ratio of the measured surfaces of the powders is 2.84. This indicates that on both powders the adsorption of hydrogen per sq. cm. of the surface is practically identical: at saturation, powder 9799 adsorbs 5.38 × $10^4$ hydrogen molecules per sq. cm., compared with 5.52 × $10^4$ per sq. cm for powder 9798. Considering that 1 sq. cm. of a tungsten surface contains 10.07 to 14.24 × $10^{14}$ tungsten atoms,[21] we have to conclude that, at the saturation, one hydrogen molecule is adsorbed per two tungsten-atoms, or one hydrogen atom per one tungsten-atom, in the surface of the metal.

TABLE V

Slopes = log $p$/log $A$

| Temp. (in °C.) | For coverings > 0.008 $S$ Powder 9798 | For coverings > 0.008 $S$ Powder 9799 | For coverings < 0.008 $S$ Powder 9799 |
|---|---|---|---|
| −194 | (67.4) | Not measd. | No exptl. pts. |
| − 73 | (24.1) | Not measd. | No exptl. pts. |
| 0 | 16.85 | 16.41 | No exptl. pts. |
| 100 | 10.88 | 10.74 | No exptl. pts. |
| 200 | 7.80 | 7.36 | No exptl. pts. |
| 300 | 5.80 | 5.40 | No exptl. pts. |
| 400 | 4.04 | 4.30 | 2.02 |
| 500 | 3.08 | 3.04 | 2.04 |
| 600 | 2.30 | 2.32 | 1.98 |
| 650 | 2.09 | 2.23 | 2.00 |
| 700 | 1.85 | 1.85 | 2.06 |
| 750 | 1.71 | 1.73 | 2.03 |

Powder 9799, with its larger surface, allowed one to carry out additional measurements in the range of "highly dilute" surface coverings. Whereas for powder 9798 all the measured points, except a very few taken at 600° and higher temperatures, correspond to coverings of the metal surface with hydrogen of more than 0.008 of the saturation value $S$, the 400°-isotherm of powder 9799, and all the higher temperature isotherms of this powder contain many points which correspond to surface coverings below 0.008 $S$. From Fig. 5, which shows the log $A$/log $p$ plot for powder 9799, it can be seen that these isotherms consist of two parts: above coverings of about 0.008 $S$, the slopes are practically identical with those found for powder 9798, whereas below 0.008 $S$ they are parallel with each other with the common slope $\alpha = 2$ (Table V). We shall see later that the parallel course of the logarithmic isotherms at these very sparse surface coverings, and their fan-like convergence at higher coverings, permit one to draw conclusions as to the heats of adsorption and to the state of the adsorbed gas, in this range of "highly diluted" adsorption.

A characteristic feature of the hydrogen adsorption on a bare tungsten surface is the wide spread of the surface fractions which are covered with the adsorbed gas, at the same equilibrium pressures, at different temperatures (Table VI). The spread is the larger the smaller the pressure.

TABLE VI

ADSORBED AMOUNTS IN PER CENT. OF SATURATION VALUE $S$ (= COVERED FRACTIONS OF THE SURFACE), AS A FUNCTION OF THE EQUILIBRIUM PRESSURES AT VARIOUS TEMPERATURES

| Equilibrium pressure in mm. | Temperatures in °C. 0 | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 750 |
|---|---|---|---|---|---|---|---|---|---|
| 1 × $10^{-5}$ | .. | .. | 4.4 | 0.8 | .. | .. | ... | .. | ... |
| 1 × $10^{-4}$ | 21.0 | 15.5 | 7.5 | 3.3 | 0.9 | .. | ... | .. | ... |
| 1 × $10^{-3}$ | 23.5 | 17.5 | 10.0 | 4.6 | 1.8 | 0.6 | ... | .. | ... |
| 1 × $10^{-2}$ | 25.5 | 19.0 | 12.0 | 6.5 | 3.1 | 1.2 | 0.4 | 0.15 | ... |
| 1 × $10^{-1}$ | 29.5 | 23.5 | 16.0 | 10.0 | 5.6 | 2.4 | 0.9 | 0.5 | 0.2 |
| 1 | 33.0 | 27.5 | 20.5 | 14.0 | 9.5 | 5.0 | 2.4 | 1.5 | 0.8 |
| 10 | 38.0 | 32.5 | 26.5 | 20.0 | 16.0 | 10.5 | 7.0 | 4.5 | 2.9 |

Still more pronounced is the spread of the equilibrium pressures for a given fractional covering of the surface, at different temperatures (Table VII). Here, too, the spread declines with closer approach to higher coverings.

We see that, at 0° and at a pressure of $10^{-4}$ to $10^{-3}$ mm., the adsorption of hydrogen on outgassed tungsten amounts to about 20 to 25% of the saturation value. The uptake of such a

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(21) For the (100) plane and the (110) plane, respectively, of the tungsten lattice.

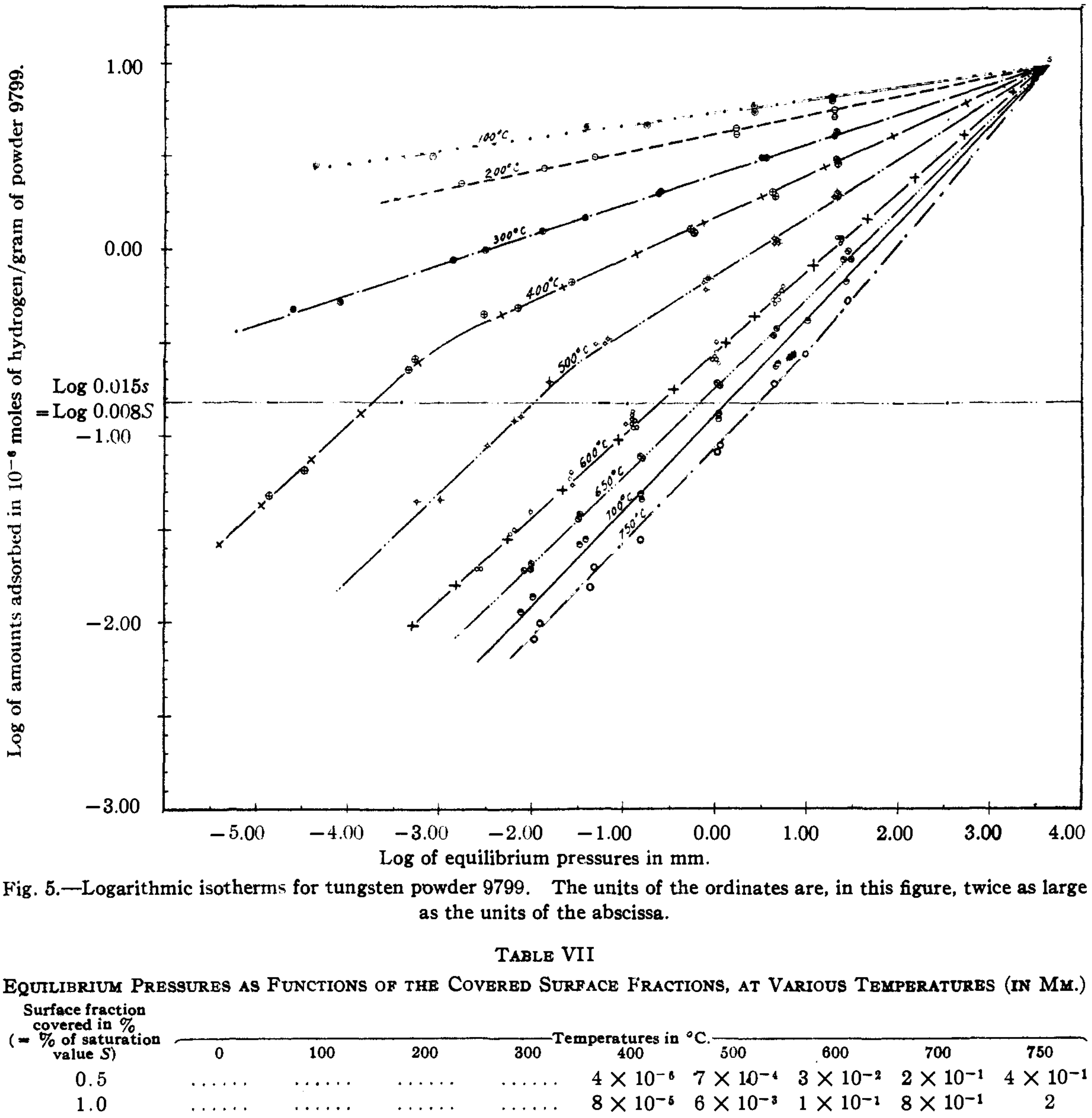

Fig. 5.—Logarithmic isotherms for tungsten powder 9799. The units of the ordinates are, in this figure, twice as large as the units of the abscissa.

TABLE VII

EQUILIBRIUM PRESSURES AS FUNCTIONS OF THE COVERED SURFACE FRACTIONS, AT VARIOUS TEMPERATURES (IN MM.)

| Surface fraction covered in % (= % of saturation value $S$) | Temperatures in °C. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 750 |
| 0.5 | ...... | ...... | ...... | ...... | $4 \times 10^{-6}$ | $7 \times 10^{-4}$ | $3 \times 10^{-2}$ | $2 \times 10^{-1}$ | $4 \times 10^{-1}$ |
| 1.0 | ...... | ...... | ...... | ...... | $8 \times 10^{-5}$ | $6 \times 10^{-3}$ | $1 \times 10^{-1}$ | $8 \times 10^{-1}$ | 2 |
| 2.5 | ...... | ...... | ...... | ...... | $4 \times 10^{-3}$ | $1 \times 10^{-1}$ | 1 | 5 | 8 |
| 5.0 | ...... | ...... | $3 \times 10^{-6}$ | $2 \times 10^{-3}$ | $8 \times 10^{-2}$ | 1 | 5 | 18 | 26 |
| 10.0 | ...... | $7 \times 10^{-6}$ | $1 \times 10^{-3}$ | $1 \times 10^{-1}$ | 2 | 8 | 23 | 50 | ...... |
| 25.0 | $5 \times 10^{-3}$ | $2 \times 10^{-1}$ | 6 | 33 | ...... | ...... | ...... | ...... | ...... |
| 37.5 | 8 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... |

large quantity of the gas at a very low equilibrium pressure is in contrast to the course of the usually described adsorption isotherms[22] which show a linear relationship between the amounts adsorbed and the pressures, in the range of low equilibrium pressures.[23] In this respect, our measurements agree, at least qualitatively, with the results obtained by J. K. Roberts[24] for the adsorption of hydrogen on a highly outgassed tungsten wire. According to Roberts, the tungsten surface is practically completely covered by the adsorbed gas at room temperature, and at a hydrogen pressure of about $10^{-4}$ mm. The saturation value, derived from his experiments, is the same as our value, namely, one hydrogen molecule adsorbed per two tungsten atoms of the metal

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(22) Comp., *e. g.*, Smithells, *loc. cit.*

(23) Even if we assume that the adsorption at 0° and 1 mm. pressure would represent as much as 80% of the saturation value, it would amount to only 0.08 to 0.008% of the saturation value at $10^{-3}$ to $10^{-4}$ mm. if there would exist, between these pressures, the linear relationship mentioned above.

(24) J. K. Roberts, *Proc. Roy. Soc.* (London), **A152**, 445, 477 (1935); **A161**, 141 (1937); J. K. Roberts, "Some Problems in Adsorption," Cambridge University Press, 1939.

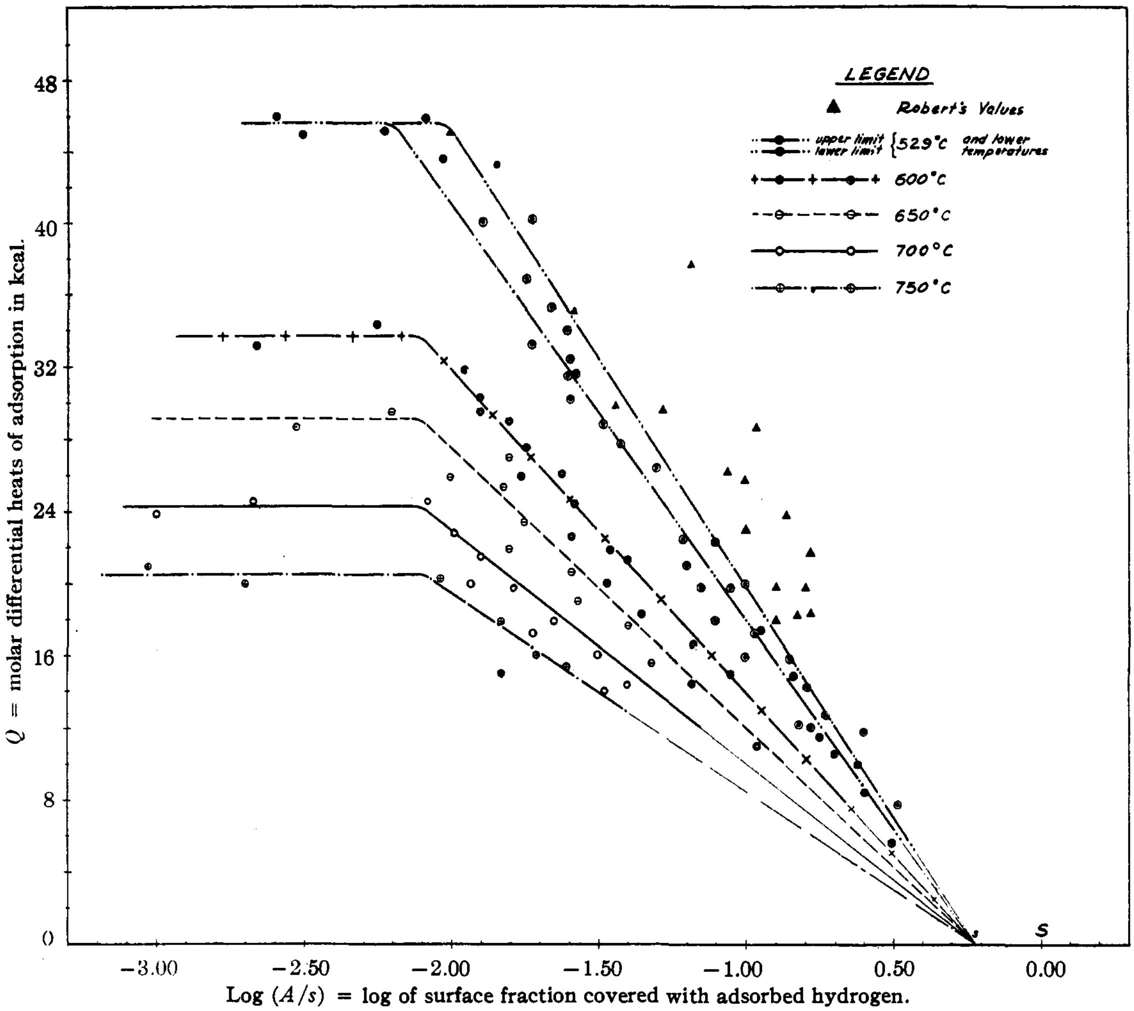

Fig. 6.—The values found by Roberts are entered at $(A/s)$ values which are smaller by a factor of 4.5, than the $(A/s)$ values calculated by Roberts (see text).

surface. In spite of this agreement, however, there exists a discrepancy between Roberts' and our results insofar as, according to our experiments, the saturation of the adsorbent is reached only at high pressures whereas Roberts concludes that saturation is already established at $10^{-4}$ mm. pressure. In order to explain this discrepancy, it has only to be remembered that, in Roberts' experiments, (1) the total adsorbing surface and, hence, the amounts of adsorbed gas to be measured, was smaller than the surfaces employed in our experiments by a factor of about $10^5$; that (2) the amounts of hydrogen adsorbed at saturation were determined by Roberts by an indirect method,[25] and that (3) the "true" surface of the adsorbing wire (including its "molecular roughness") was not measured directly. In view of these differences in the experimental method, the results of both sets of experiments can be considered as being compatible with each other. Complete agreement would be reached if one assumes that the true "molecular" surface of the tungsten wire used as adsorbent by Roberts was larger by a factor of about 4.5 than its geometrical surface. It is not unlikely that the wire was "roughened up" to a considerable extent by the outgassing operation (alternating heating to about 2000°K., and cooling to room temperature, with simultaneous diffusion of the occluded gases through the crystallites of the wire). It is well known that, by such a treatment, metal surfaces are disintegrated, to a considerable extent. As to the factor 4.5 for the ratio of the true to the geometrical surface, we can see from a comparison of the surface values of our powders (Table I) that the microscopic counting method which is based on the summing up of the geometric surfaces of the individual particles, yields actually

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(25) This indirect method, based on measurements of the differential heats of adsorption with increased covering of the surface of the tungsten wire, becomes necessarily less reliable the closer the adsorption approaches saturation, because of the slow increase of the adsorbed amounts in this range of pressures, and of the sharp decline of the adsorption heats with increasing covering of the tungsten surface with hydrogen (see later).

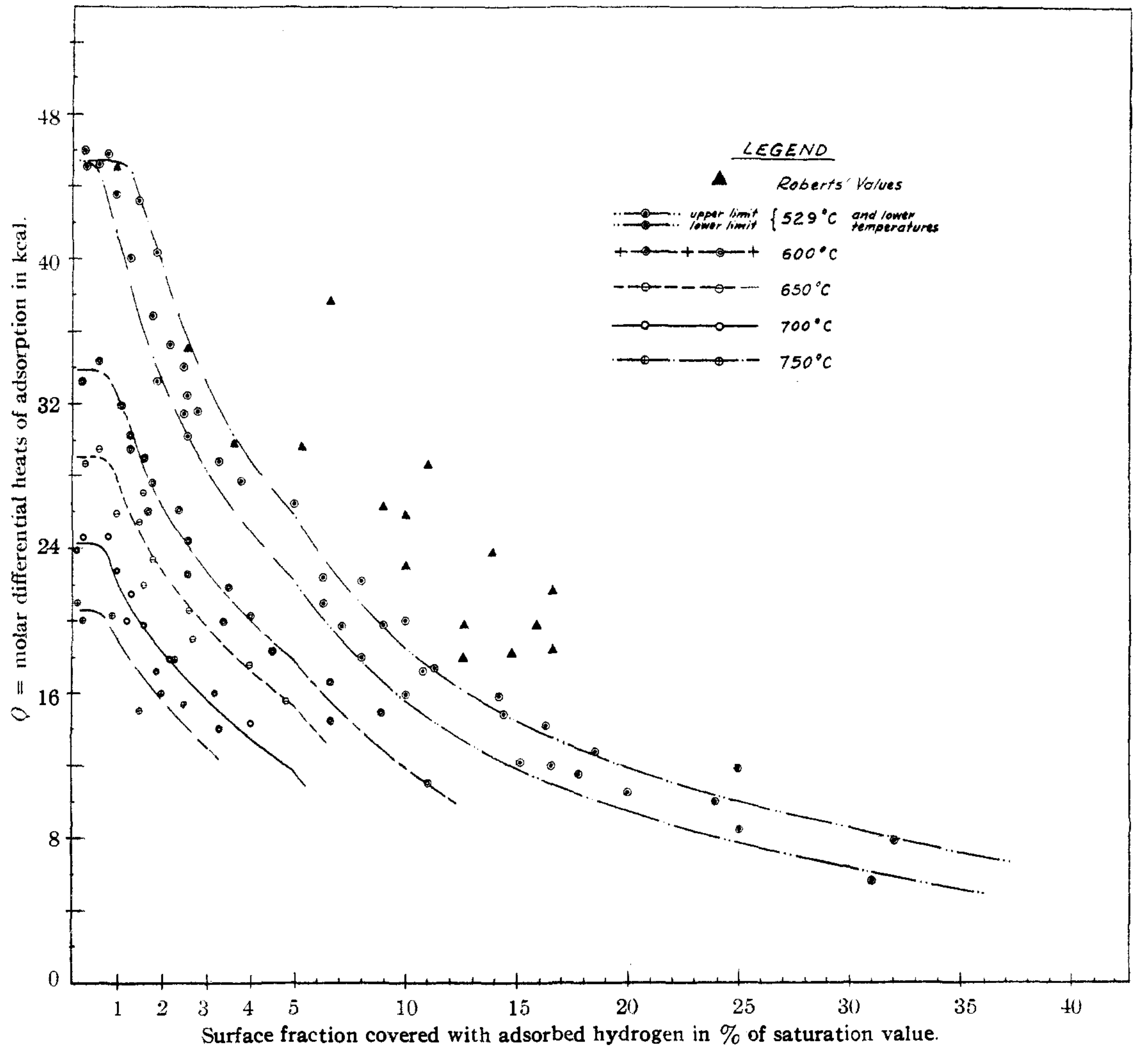

Fig. 7.—The scale of the abscissa is reduced above 5% of surface covering. The values found by Roberts are entered at surface fractions which are smaller, by a factor of 4.5, than the values calculated by Roberts (see text).

values which are smaller than the true molecular surfaces by factors ranging from 2.2 to 6.07.[26]

From the measured adsorption equilibria, the differential heats of adsorption were calculated, as a function of the covering of the surface, by means of the Clausius–Clapeyron equation.[27] Fig. 6 shows, in a logarithmic scale, and Fig. 7, in ordinary scale, the differential heats of adsorption per mole of adsorbed hydrogen. We see that, at very low surface coverings (below about 0.008 $S$), the heats of adsorption are constant and amount to about 46,000 cal./mole of adsorbed hydrogen. With the surface covering increasing above 0.008 $S$, the differential heats of adsorption $Q$ decrease rapidly, according to

$$Q = \gamma \log (s/A) \qquad (1)$$

where $s = 0.55\,S$ = amount of hydrogen adsorbed at the extrapolated point of intersections of the logarithmic isotherms, $A$ is the amount adsorbed with the differential heat of adsorption $Q$, $\gamma$ is a constant. This equation conforms well with the experimental data, within the range of surface coverings above 0.008 $S$ up to the highest adsorption values for which measurements could be carried out (0.35 $S$ = 0.64 $s$). Equation (1) can also be expressed in the form

$$Q = Q' - \gamma \log (A/A') \qquad (2)$$

where $Q'$ is equal to the constant heat of adsorption (46,000 cal.) at coverings $\leq A'$, and $A'$ is equal to the "critical surface covering" of 0.008 $S$.

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(26) From the rate of evaporation of a tungsten wire, F. J. Wilkins (*Nature*, **125**, 236 (1930)) concludes that the true surface of the wire exceeds its apparent surface by the factor 5.

(27) In several cases described in the literature, direct calorimetric measurements of heats of adsorption checked well with the values derived from applying the Clausius–Clapeyron equation to the equilibrium pressures which exist, for the same surface coverings, at the various temperatures. Compare, *e. g.*, R. A. Beebe and H. S. Taylor, THIS JOURNAL, **46**, 43 (1924), and Rideal, *J. Chem. Soc.*, **121**, 309 (1922), and Iijima, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **22**, 285 (1933); further, Garner and Maggs, *Trans. Faraday Soc.*, **32**, 1744 (1936), and Garner and Veal, *J. Chem. Soc.*, 1436 (1935); (private communication by Mr. R. A. Beebe).

For all the temperatures between − 194 and about 530°, the curve of the heats of adsorption, as a function of the surface coverings, remains unchanged. For temperatures above 530°, however, the quantity $\gamma$ of equations (1) and (2) decreases considerably the higher the temperature rises above 530°: the curves of the differential heats of adsorption are shifted, over their entire lengths, toward increasingly lower levels. We shall discuss in detail the method of calculation and the trend of the heats of adsorption in connection with the general discussion of our results given in the following paper. It may be sufficient to mention here that Roberts found, at room temperature, an initial heat of adsorption of about 45,000 cal./mole of hydrogen, compared with our corresponding value of 46,000 cal./mole of hydrogen. He finds that, with increasing covering of the surface, the heats of adsorption decrease approximately linearly, and that they reach at that covering which Roberts considers to be equivalent to "saturation" of the adsorbent, the value of about 18,000 cal./mole of hydrogen.[28]

Figures 6 and 7 show that the heats of adsorption found by Roberts lie, in the average, somewhat higher than our values. In spite of this deviation, one can conclude that Roberts' heat of adsorption at "saturated adsorption" corresponds, if related to our heat curve, to a surface covering of approximately 10 to 20%. This confirms, at least roughly, our previous conclusion drawn from the amount of hydrogen adsorbed at $10^{-4}$ mm. pressure. Furthermore, it can be seen that the partial segment of the total heat curve measured by Roberts easily can be interpreted as a linear decrease of the heats of adsorption with increasing surface covering. Only the fact that our measurements cover an appreciably larger range makes it possible to see that the heats of adsorption do not decrease in direct proportionality to $A$, but to log $(A/A')$. In this connection, one has to keep in mind that the values of the differential heats of adsorption derived from the wire experiments were, necessarily, determined only in first approximation.[28] Regardless of the interpretation of the "saturation value" found in the wire experiments, the fact that the initial heats of adsorption derived by the two completely different methods are close to each other, can be added to the other evidence which makes it almost certain that the tungsten surfaces of our thoroughly outgassed powders were in a similar state of purity to the surface of the tungsten wire which was outgassed by "flashing it out," at very high temperatures, in Roberts' investigation.

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## Summary

1. The adsorption of hydrogen on metallic tungsten is measured for equilibrium pressures between $1 \times 10^{-5}$ and 30 mm. and at temperatures from − 194 to 750°.

2 As adsorbents, tungsten powders are used with surfaces of about 7000 to 20,000 sq. cm. per gram. These "true" surfaces were determined by the method of Emmett and Brunauer (adsorption of nitrogen at low temperatures), and are greater than the "geometric" surfaces (evaluated by a microscopic counting method) by factors between 2.2 and 6.07.

3. Previous to the adsorption measurements, the tungsten powders are reduced in a hydrogen stream at 750°, and subjected to a thorough outgassing procedure which consists in heating them at 750°, in a high vacuum, for thirty-five to fifty hours. The progress of the outgassing is measured by determining the residual gas evolution from the powders into a high vacuum, at 750°, and by registering the gas evolution from the powders at 750° into a high vacuum, after they have been kept for periods of about fifteen hours at room temperature, in a high vacuum. The minimum values of these residual gas evolutions being reached, they remain constant, in spite of further continuation of the outgassing. In this stage, the powders show well reproducible values of hydrogen adsorption. The residual gas evolutions are negligible compared with the amounts of hydrogen adsorbed, even at low pressures and high temperatures.

4. The adsorption measurements can be well reproduced with the same powder specimen, after repeated outgassing, as well as with another specimen of the same powder sample. This applies also for adsorption runs carried out in two different apparatus which were calibrated independently.

5. The adsorption of hydrogen on the outgassed tungsten powders is characterized by the uptake of relatively large amounts of the gas, at

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(28) In Roberts' experiments, the heats of adsorption (not exactly the differential heats, but integrals of heats over a certain fraction of the surface covering) were, by an ingenious method, determined from the increase of the temperature of the tungsten wire, this increase being caused by successive adsorptions of small amounts of hydrogen admitted into the adsorption chamber. These temperature increases were measured by means of the corresponding changes of the electric resistance of the wire. They amounted, as a simple calculation shows, to only about 1/1000 to 1/10,000°. In view of the smallness of this effect, only a rough agreement can be expected between the values found by this "direct" method, and the values derived from our measurements. This applies especially for somewhat higher equilibrium pressures ($10^{-4}$ to $10^{-3}$ mm.), at which the temperature increase of the wire, by a given amount of heat of adsorption, will be greatly influenced by the heat conductivity of the surrounding hydrogen atmosphere.

low pressures (about 25% of the saturation value, at $10^{-4}$ mm. equilibrium pressure and 0°). The amounts of hydrogen adsorbed, at the same equilibrium pressure, show a wide spread for different temperatures, particularly in the low pressure region.

6. Extrapolation of the adsorption isotherms to high pressures leads to a saturation value of adsorption corresponding to the covering of the tungsten with 1 hydrogen molecule per 2 tungsten atoms in the metal surface.

7. The amounts of hydrogen adsorbed per 1 sq. cm. of the tungsten surface at a given temperature and pressure are identical, within the limits of experimental error, for two different powders the surfaces of which differ by the factor 3.

8. If the adsorbed amounts $A$ are plotted against the equilibrium pressures $p$, in a log $A$/log $p$ diagram, the isotherms are very nearly straight lines showing different slopes log $p$/log $A$. The slopes range from 1.75 for the 750° isotherm to about 78.0 for the $-194°$ isotherm. The logarithmic isotherms converge, fanwise, toward a point of common intersection in the region of high pressures.

9. With a powder of high specific surface, measurements were carried out which reached for temperatures of 400° and above into the range of very sparse coverings of the adsorbent corresponding to less than 0.8% of the saturation value $S$. In this range, the logarithmic isotherms are parallel to each other, and have the common slope (log $p$/log $A$) = 2.

10. By means of the Clausius–Clapeyron equation, the differential heats of adsorption were evaluated, for increasing coverings of the tungsten surface with adsorbed hydrogen. In the "highly diluted" range of $<0.008\ S$, the adsorption heat is independent of the amount adsorbed, within the temperature range of $-194$ to about 530°, and amounts to about 46,000 cal./mole of hydrogen. At coverings $>0.008\ S$, the heats of adsorption decrease rapidly with the increasing covering of the surface, proportional to $Q' - \log(A/A')$; $Q'$ and $A'$ being constants. The entire curve of the heats of adsorption as a function of the surface covering, is shifted to lower levels at temperatures exceeding about 530°.

11. It can be shown that the measurements of J. K. Roberts of hydrogen adsorption on a tungsten wire agree qualitatively and, to a certain extent, quantitatively with the results mentioned above if it is assumed that the true molecular surface of the adsorbent wire exceeded its geometrical surface by the factor 4 5.

12. This agreement, together with other evidence, makes it very likely that the surfaces of the outgassed powders consisted practically completely of the free metal.

13. A discussion of these results, and of their bearing on views on the mechanism of adsorption, will be represented separately.

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# The Adsorption of Hydrogen on Tungsten. II

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In a previous paper,[2] the adsorption of hydrogen on the surface of thoroughly outgassed tungsten powders was described, for equilibrium pressures ranging from $10^{-5}$ to 30 mm., and for temperatures from $-194$ to 750°. From the amounts $A$ which were adsorbed at the various pressures $p$ and temperatures $T$, the differential heats of adsorption $Q$ were computed. The amounts of hydrogen adsorbed per sq. cm. of the metal surface ranged from about $1 \times 10^{12}$ hydrogen molecules, at the lowest equilibrium pressures measured ($1 \times 10^{-6}$ to $1 \times 10^{-5}$ mm.), up to about $200 \times 10^{12}$ hydrogen molecules, at pressures of the order of magnitude of 30 mm. Measurements with two different tungsten powders of similar origin but with different specific surfaces (ratio 1:3) showed that the amounts of hydrogen adsorbed per unit of surface, at a given temperature and equilibrium pressure, were the same for both adsorbents, within the limits of experimental error.

**Main Part of the Isotherms.**—In the following discussion of these results, we shall deal first with the *main part* of the isotherms, corresponding to surface coverings from about 0.8% of the saturation value up to the highest adsorption values reached (about 35% of the saturation value). The remaining part of the measured isotherms which corresponds to the "highly diluted range" of adsorption (from the lowest coverings which were measured, about 0.25%, up to about 0.8% of the saturation value) will be discussed separately. For these very sparse surface coverings, another relationship exists between the adsorbed quantities and the equilibrium pressures than was found for the denser coverings within the main parts of the isotherms.

The discussion is greatly simplified if it is based on the "logarithmic isotherms," *i. e.*, on diagrams which show the experimental results plotted as log $A$ against log $p$. In such a diagram, all the

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[2] Frankenburg, THIS JOURNAL, **66**, 1827 (1944), hereafter cited as "I."